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(54) METHOD FOR PROTECTION OF EVAPORATOR HEATING ELEMENTS FROM CORROSION

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This invention relates to methods for corrosion protection of heating elements in evaporators operating in alkaline media, for example, in evaporators used for the manufacture of caustic soda. The aforesaid evaporators are intended for carrying out the processes of concentrating (evaporating) alkaline solutions under elevated temperatures and diverse service conditions, such as natural or forced circulation of alkaline solutions, various pressures of the heat carrier (usually steam), and erosion due to the circulation of alkaline pulp containing a significant proportion of solid matter.

During the service life of evaporating-plant equipment the principal elements of the evaporators, viz. the heating tubes, undergo severe deterioration under the effect of corrosive alkaline media and also suffer from pronounced erosion and corrosion, particularly where evaporator operation involves forced circulation of alkaline solutions containing different admixtures.

Known in the art are many methods for corrosion protection of heating elements of evaporators intended for handling alkaline media.

For example, use is made of heating elements manufactured from corrosion-resisting materials, e.g. nickel, nickel-base alloys, or high-alloy austenitic steels which contain, apart from chromium, molybdenum and other alloying elements, also an adequately high proportion of nickel, viz. 25 to 28%.

In some instances recourse is had to equip-

ment made from ordinary steel, provided inhibitors, such as sodium nitrate or saccharose, are incorporated into the alkaline corrosive medium.

It is further known to effect corrosion protection by the anode polarization technique.

The known methods of corrosion protection suffer from the drawback of resorting to heating elements made from nickel, which is an expensive metal, or from a nickel-base alloy and nickel containing steels, the employment of nickel for this purpose being particularly undesirable in view of the constantly growing consumption of nickel for other purpose such as the production of heat-resistant and high-temperature alloys. This situation has prompted world-wide studies directed to the development of steels and alloys containing a lower percentage of nickel and to finding conditions, under which steels containing little or no nickel would exhibit corrosion-resisting properties for specific applications.

The aforesaid studies are essentially aimed at minimizing the consumption of nickel for the equipment to be used in large-tonnage manufacturing processes, among which mention may be made of caustic soda production, under temperature conditions which do not necessarily require heat-resistant materials.

The known methods involving the use of corrosion inhibitors are not invariably effective, particularly where the equipment to be protected is made from plain carbon steel. The employment of anodic protection in heating elements is likewise inefficient due to the principles on which the design of these element is based.

Accordingly to the present invention, the heating elements are made from steel containing 23 to 30% by weight chromium as the sole alloying element, the steel undergoing passivation under the effect of an inhibitor, sodium chlorate, present in a concentration of 0.05—1 g/l in an alkaline solution at a temperature of 90 to 450°C.

The protective film formed as a result of interaction between the high chromium steel

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and a chlorate-containing alkaline solution exhibits high adhesiveness to the base metal and is also noted for its good resistance to the erosive effects of a rapid stream of hot alkaline liquid flow (rate, 4 to 5 m/sec) containing about 20% of solid phase, e.g. sodium chloride in the manufacture of caustic soda.

No positive addition of the corrosion inhibitor (sodium chlorate) in alkaline solution is required when manufacturing caustic soda, since sodium chlorate is a by-product of caustic soda manufacture and is present in the alkaline solution in an amount of 0.05 to 1 g/l which is adequate for chromium steel passivation.

Where no sodium chlorate is present in alkaline solution, the above specified amount of the inhibitor should be added to the solution being handled.

Currently available evaporator housings manufactured from chromium-nickel steel containing 18% Cr and 10% Ni can be used

in conjunction with the heating elements according to the present invention, since the contact between the Cr/Ni steel and the high-chromium steel (e.g. containing 25% Cr) is permissible and a heating element may be assembled by mounting high-chromium steel tubes in a housing made from chromium-nickel steel.

It is preferable to use also high-chromium steel or plain carbon steel clad with high-chromium steel for fabricating the framework of the heating elements.

Data listed in Table 1 pertain to laboratory experiments under static conditions in a 50% solution of sodium hydroxide and make it possible to evaluate the behaviour of various steel grades and of nickel in an alkaline environment at temperatures that are close to those used for the evaporation of alkaline solutions under plant conditions.

TABLE 1

Metal	Contents of sodium chlorate, g/l	Corrosion rate, mm/year		
		Temperature, °C		
		100°	120°	140°
Plain Carbon Steel	0.0	0.62	1.90	3.70
	1.0	2.8	5.1	7.9
Steel containing 18% Cr and 10% Ni	0.0	0.20	0.31	0.71
	1.0	0.44	1.20	1.90
Steel containing 18% Cr, 12% Ni and 3% Mo	0.0	0.16	0.20	0.54
	1.0	0.32	0.82	1.4
Steel containing 25% Cr	0.0	0.18	0.28	2.1
	1.0	0.021	0.08	0.08
Nickel (99.5% Ni)	0.0	0.08—0.1	0.08—0.1	0.08—0.1
	1.0	0.08—0.1	0.08—0.1	0.08—0.1

It follows from the above data that, among the steels tested, high-chromium steel is unique in that it exhibits high corrosion resistance in a corrosive alkaline medium containing sodium chlorate throughout the range of test temperatures.

Under the same conditions, plain carbon and chromium-nickel steels undergo dissolution at

a high rate, and the presence of an oxidizing component (sodium chlorate) exerts a marked accelerating effect on the rate of corrosion hence, plain carbon steel and also chromium-nickel steel and chromium-molybdenum steel at elevated temperatures, have virtually no corrosion resistance.

High-Chromium steel is noted for its high

corrosion resistance under the conditions specified hereinbefore and is not inferior to nickel, a scarce metal, in this respect.

Similar results confirming the high corrosion-resistance of high-chromium steel con-

taining 25 to 28% of chromium were obtained under conditions of caustic soda concentration, in the presence of sodium chlorate as an inhibitor, where the sodium hydroxide content rose from 44—45% to 96% during the test period.

TABLE 2

Steel grade	Starting specimen weight g.	Sodium chlorate content g/l	Temperature °C	Specimen weight loss during test period 180 hrs, in grams
Steel containing				
25—28% Cr	8.3476	0.0	340—350	4.3209
— " "	8.2192	0.0	340—350	4.7269
— " "	8.3326	1.0	340—350	0.2214
— " "	9.6231	1.0	340—350	0.2026

It is apparent from the data of Table 2 that even at high temperatures the inhibiting action of sodium chlorate is retained, the rate of the specimen corrosion in melted alkali in the presence of sodium chlorate being 20—23 times lower than without sodium chlorate.

With reference to chromium steel containing a lower percentage of chromium (13 and 17% Cr), these materials retain an adequate cor-

rosion resistance and undergo passivation in a 30% solution of sodium hydroxide containing sodium chlorate. Table 3 summarizes the results of laboratory tests on chromium steel specimens containing 13% and 17% Cr. Corrosion resistance was evaluated at different temperatures in a 30% solution of sodium hydroxide containing sodium chlorate.

TABLE 3

Steel grade	Content of sodium chlorate g/l	Corrosion rate, mm/year			
		Temperature, °C			
		100°	120°	140°	160°
Steel containing	0.0	0.6	1.3—1.8	—	—
13% Cr	0.35—0.45	0.19	0.77	—	—
Steel containing	0.0	0.24	0.45	0.60	—
17% Cr	0.35—0.45	0.07	0.080	0.15—0.20	0.68

It is apparent from the data of Table 3 that increasing the chromium content of the steel results in broadening the range of temperatures at which this type of steel is able to undergo passivation in a 30% solution of sodium hydroxide.

For a better understanding of the present invention presented hereinbelow are examples of plant tests on specimens of various metals used in the tubes of heating elements in the evaporators of caustic soda plants. Tests were also conducted on tubes made from appropriate metals and mounted in the framework of heating elements in evaporators used for evap-

orating electrolytic caustic soda from diaphragm cells.

EXAMPLE 1

Plant tests were conducted on specimens made from diverse steel grades, viz. chromium-nickel steel containing 18% Cr and 10% Ni; chromium-nickel-molybdenum steel containing 18% Cr, 12% Ni, and 3% Mo; and chromium steel containing 17% and 25% Cr; in a medium consisting of a 42% solution of sodium hydroxide, in which the content of sodium chlorate was 0.8 to 1 g/l and the content of sodium chloride was 20 g/l, the temperature of the heating steam being 120°C.

Apart from the corrosive action exerted by the medium the test specimens underwent erosion caused by high-speed stream of alkaline pulp (Flow rate 4 to 5 m/sec).

- 5 Under the above specified conditions, the steel specimens are corroded at the following rate, in millimetres per year:—
- | | |
|---|------|
| Steel containing 18% Cr and 10% Ni | 2.5 |
| 10 Steel containing 18% Cr, 12% Ni, and 3% Mo | 1.8 |
| Steel containing 25% Cr | 0.06 |
| Steel containing 17% Cr | 1.2. |

EXAMPLE 2

- 15 Plant tests were conducted on tubes made from plain carbon steel; chromium-nickel steel containing 18% Cr and 10% Ni; chromium-nickel-molybdenum steel containing 18% Cr, 12% Ni, and 3% Mo; and chromium steel
- 20 containing 25% Cr; the test conditions being identical to those of Example 1.

The tubes made from the aforesaid materials were found to have the following service life, in months:—

- | | |
|--|--------|
| 25 Plain Carbon steel tubes | 2 to 3 |
| chromium-nickel and chromium-nickel-molybdenum steel tubes | 6 to 8 |

- 30 In tubes made from chromium steel, continuous service resulted in neither corrosion damage of the tubes nor diminution of the tube wall thickness. At the points at which the tubes were welded to the tube framework of the heating elements no leaks developed.

- 35 The present method may find employment for corrosion protection of not only evaporator heating elements, but also for corrosion protection of equipment handling alkaline media under the aforesaid conditions in diverse chemical processes.

WHAT WE CLAIM IS:—

- 40 1. A method of corrosion protection of heating elements in evaporators intended to handle alkaline solutions, wherein use is made of heating elements manufactured from steel containing 23 to 30% by weight chromium as the sole alloying element, the steel being capable of undergoing passivation under the effect of an inhibitor, sodium chlorate, present in the alkaline solution at a concentration of 0.05 to 1 g/l, the temperature of the alkaline solution being 90 to 450°C.
- 45 2. A method of concentrating an alkaline solution, comprising evaporating the alkaline solution at a temperature of 90 to 450°C in the presence of sodium chlorate at a concentration of 0.05 to 1 g/l by means of heating elements manufactured from steel containing 23 to 30% by weight chromium as the sole alloying element, the steel being capable of undergoing passivation under the effect of the inhibitor, sodium chlorate.
- 50 3. A method as claimed in claim 1 or claim 2, in which the alkaline solution is caustic soda solution.
- 55 4. A method as claimed in any of the preceding claims, substantially as described herein.
- 60 5. An evaporator for handling alkaline solutions, comprising heating elements manufactured from steel containing 23 to 30% by weight chromium as the sole alloying element, the steel being capable of undergoing passivation under the effect of an inhibitor, sodium chlorate, present in the alkaline solution at a concentration of 0.05 to 1 g/l, the temperature of the alkaline solution being 90 to 450°C.
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